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Impact to Underground Sources of Drinking Water and Domestic Wells from Production Well Stimulation and Completion Practices in the Pavillion, WY Field

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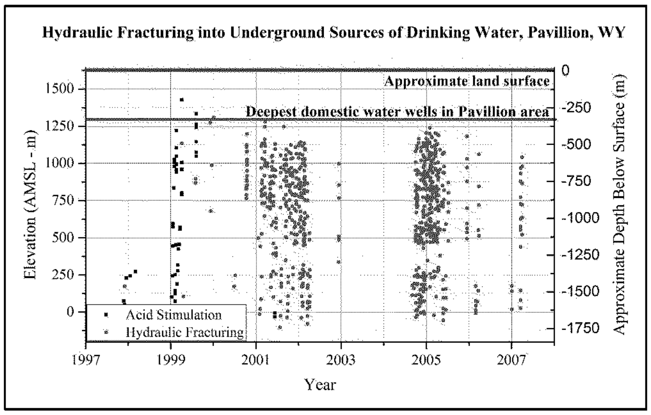

ABSTRACT

A comprehensive analysis of available data and reports was conducted to evaluate impact to Underground Sources of Drinking Water (USDWs) as a result of acid stimulation and hydraulic fracturing in the Pavillion, WY Field. Although injection of stimulation fluids into USDWs co6located with gas6 bearing sandstone units in the Pavillion Field was previously documented by EPA, impact to USDWs as a result of this activity was not evaluated. Concentrations of sodium, potassium, and chloride in produced water samples well above levels expected in the Wind River Formation, leakoff into formation media, and likely loss of zonal isolation during some stimulation stages, indicates that impact to USDWs has occurred. Since, hydraulic fracturing is largely exempted from the Safe Drinking Water Act, impact to USDWs as documented here for the first time, is currently allowable under federal law in the United States. Elevated levels of chloride and detection of organic compounds in two monitoring wells installed by EPA indicates upward solute migration to depths of current ground6water use. Detection of diesel range organics and other organic compounds in domestic wells < 600 m from unlined pits used prior to

the mid61990s to dispose diesel6fuel based drillingmud and production fluids suggest impact to domestic wells from pit disposal practices.

INTRODUCTION

Between 2005 and 2013, natural gas production in the U.S. increased by 35% largely due to unconventional gas production in shale and tight gas formations[1]. Between 2013 and 2040, natural gas production is expected to increase another 45% with production from tight gas formations in particular increasing from 4.4 to 7.0 trillion cubic feet (59%) with most growth from the Gulf Coast and Dakotas/Rocky Mountain regions[1]. Tight gas formations already account for 26% of total natural gas production in the United States today[2].

In the U.S. Code of Federal Regulations (CFR), there are two federal statutes for protecting ground6water resources for present and future use relevant to oil and gas extraction – “Underground Source of Drinking Water” (USDW) and “usable water.” A USDW is defined in 40 CFR 144.3 as an aquifer that currently supplies drinking water for human consumption or a public water system or that contains sufficient quantity to supply a public water system, contains ≤ 10,000 mg/L total dissolved solids (TDS), and is not an exempted aquifer. The separate “usable water” designation applies to lands containing federal or tribal mineral rights regulated by the Bureau of Land Management (BLM). In BLM Onshore Oil and Gas Order No. 2, usable water is defined as water containing ≤ 10,000 mg/L TDS – a definition maintained in the March 2015 BLM rule on hydraulic fracturing (43 CFR 3160). With an exception for use of diesel fuel, the Energy Policy Act of 2005 exempted hydraulic fracturing from the Safe Drinking Water Act. Thus, outside federal and tribal lands, injection of stimulation fluids not containing diesel fuel into USDWs and presumably any associated impact as a result of injection is currently allowable under federal law in the United States.

EPA[3] documented the widespread use of hydraulic fracturing in USDWs co6located in formations used for coal bed methane (CBM) recovery. EPA[3] acknowledged likely local ground water contamination as a result of this activity but concluded that dilution, adsorption, and biodegradation would likely reduce contaminant concentrations to safe levels prior to reaching domestic wells which were generally shallower than production wells. Recently though, EPA[4] stated that injecting stimulation fluids directly into USDWs "presents an immediate risk to public health because it can directly degrade groundwater, especially if the injected fluids do not benefit from any natural attenuation from contact with soil, as they might during movement through an aquifer or separating stratum."

To our knowledge, the extent of well stimulation into USDWs co6located with tight gas deposits has not been previously investigated. Ground6water investigations related to well stimulation are typically limited to sampling of domestic water wells. Evaluating impact to water resources is broader than impact to domestic wells alone, in that the former can occur in absence of the latter as commonly observed in investigations conducted under the Comprehensive Environmental Response and Liability Act (CERCLA).

The Pavillion Field is located east of the Town of Pavillion in Fremont County, WY, in the west6 central portion of the Wind River Basin (WRB) (Figure SI A1). The field consists of 181 production wells including plugged and abandoned wells (central portion of the Field illustrated in Figure 1) of which tribal mineral rights are applicable to more than half. Natural gas with smaller amounts of oil is conventionally and unconventionally extracted from sandstone deposits of variable permeability.

In response to complaints regarding foul taste and odor in water from domestic wells within the Pavillion Field, EPA initiated a ground water investigation in September 2008 under CERCLA[5]. EPA conducted two domestic well sampling events in March 2009 (Phase I)[5] and January 2010 (Phase II)[6]. Between June and September 2010, EPA installed two monitoring wells, MW01 and MW02, using mud rotary drilling with screened intervals 233 – 239 m and 296 – 302 m below ground surface (bgs), respectively to evaluate upward solute transport of compounds associated with well stimulation[7]. MW01 and MW02 were sampled by EPA during the Phase III (October 2011) and Phase IV (April 2011) sampling events.

In December 2011, EPA[7] released a draft report summarizing results of the Phase I6IV sampling. EPA documented ground6water contamination in surficial Quaternary unconsolidated alluvium attributable to numerous unlined pits used for disposal of diesel6oil6based (invert) drilling mud and production fluids including flowback, condensate, and produced water prior to the mid61990s. EPA[7] also documented injection of stimulation fluids into USDWs and concluded that inorganic and organic geochemical anomalies at MW01 and MW02 suggested upward solute migration of compounds to depths of current ground water use.

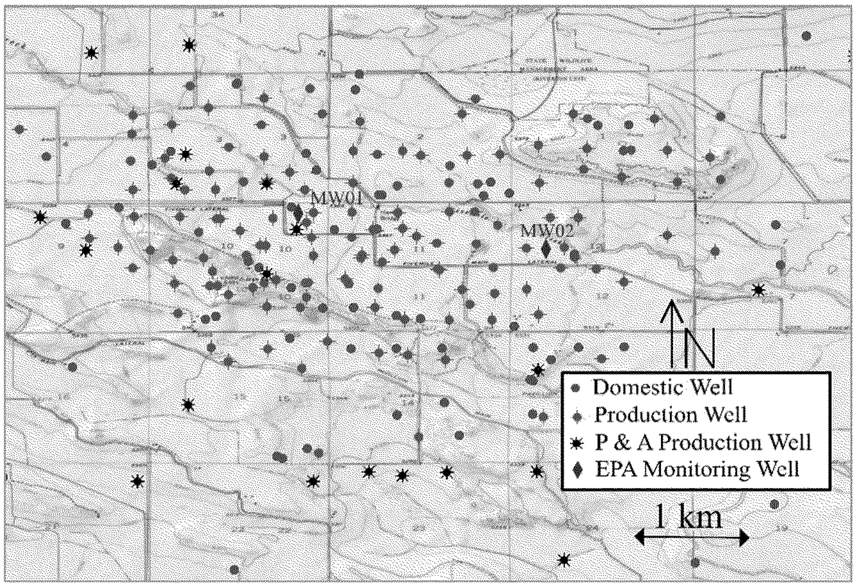

Figure 1. Central portion of the Pavillion Field illustrating locations of domestic water wells, production wells, plugged and abandoned (P&A) wells, and EPA monitoring wells (labeled). The entire Field, with labels for production and domestic wells and approximate locations of unlined pits, is illustrated in Figure SI A5.

A substantial amount of data has been collected since publication of the 2011 draft EPA report adding to an already extensive database. In April 2012 (Phase V) the EPA[8,9] split samples with the U.S. Geological Survey (USGS) at MW01[10,11] and MW02[12]. In 2014, the Wyoming Department of Environmental Quality (WYDEQ) re6sampled a subset of domestic wells previously sampled by EPA[13]. In 2014 and 2015, the Wyoming Oil and Gas Conservation Commission (WOGCC) released reports of their investigations on production well integrity[14] and surface pits[15], respectively.

We conducted a comprehensive analysis of available data and reports, including new documents, to evaluate impact to USDWs and usable water as a result of acid stimulation and hydraulic fracturing.

Although injection of stimulation fluids into USDWs co6located with gas6bearing sandstone units in the Pavillion Field was previously documented by EPA[7], the magnitude of this practice and impact on USDWs were not assessed. Moreover, despite cumulative injection of large volumes of stimulation fluids into closely spaced vertical wells characteristic of CBM and tight gas formations, a comprehensive evaluation of impact to USDWs and usable water at any specific well field has not to our knowledge been performed. Here, we undertake such an analysis for the Pavillion Field and re6examine potential upward migration of contaminants to depths of current ground water use using data released subsequent to the EPA 2011 draft report. We also evaluate potential impact to domestic wells as a result of disposal of production fluids in unlined pits.

METHODS

Sources of publically available information and data that we assembled and analyzed are summarized in the online Supporting Information (SI). Sources of EPA reports, Quality Assurance Project Plans (QAPPs), and Audits of Data Quality (ADQs) are provided in Table SI F1 along with USGS and WOGCC reports. Sources of analytical data and associated information on quality assurance and control (QA/QC) are summarized in Table SI F2. ADQs were conducted by EPA for Phase I – IV investigations to verify the quality of analytical data and consistency with requirements specified in QAPPs.

Material Safety and Data Sheets (MSDSs) of products used for well stimulation provided by the Pavillion Field operator, EnCana Oil & Gas (USA) Inc. (Encana), to EPA[16] are summarized in Table SI C3. We obtained analytical results of two rounds of domestic well sampling conducted by the WYDEQ in 2014 as the result of an information request filed to the State of Wyoming by the Powder River Basin Resource Council[13]. During the Phase V sampling event, EPA developed a gas chromatography6flame ionization6based approach to obtain a lower reporting limit (50 μg/L) for methanol compared to commercial laboratory analysis (5,000 μg/L). We obtained this dataset as the result of a Freedom of Information Act request to EPA by the Natural Resources Defense Council[17].

We reviewed over 1,000 publically available well completion reports, sundry notices, drilling reports and cement bond and variable density logs accessed from the WOGCC internet site using API search numbers to determine dates of well completion, depths of surface casing, top of original or primary cement, and numbers and depths of remedial cement squeeze jobs. Similarly, we reviewed available well completion reports and sundry notices at all production wells to document and better understand well stimulation practices. An extended summary of findings is provided in tables in SI Section C.

Additional data for produced water and well integrity collected by Encana and EPA were also examined here. Encana analyzed major ions in produced water at 42 production wells in 2007. EPA collected produced water samples at 4 production wells in 2010 and analyzed for organic compounds[6]. Encana conducted mechanical integrity and bradenhead (annular space between production and surface casing) testing between November 2011 and December 2012. In addition to sustained casing pressure at many production wells, during that period, water flowed to the surface through the bradenhead at four production wells. Aqueous analysis of bradenhead waters by Encana was limited to major ions. Production well string and brandenhead gas samples were collected for benzene, toluene, ethylbenzene, xylenes (BTEX) and light hydrocarbons. Results of these tests and analyses are summarized in SI Section D.

To evaluate the effect of purging volume on water quality, EPA collected ten samples through time (Figure SI E8) during the Phase V sampling event at MW01. Based on EPA's purging procedure, we developed a model incorporating plug flow in casing and mixing in the screened interval (SI Section E.3, Figure SI E6). Our simulations indicated that 99.997% of water exiting MW01 at the time of the first sample collection originated directly from the surrounding formation (i.e. samples contained little or no stagnant casing water). Unlike MW01, MW02 was a low flow monitoring well. During the Phase V sampling event, MW02 was repeatedly purged over a 66day period to ensure that most if not all sampled water originated from the surrounding formation (SI Section E.2, Figure SI E5). The cause of low flow is unknown but could be due to several factors, including low relative aqueous permeability due to gas flow or insufficient removal of drilling mud during well development. An extensive discussion of materials used for EPA monitoring well construction (drilling mud, well casing, cement) and likelihood of impact on sample results is provided in SI Section E.

RESULTS AND DISCUSSION

Ground Water Resources in the Pavillion Area

Gas extraction in the Pavillion Field occurs primarily from the Paleocene Fort Union and overlying Eocene Wind River Formations with hydrocarbon source rocks present in deeper Upper Cretaceous deposits. Both formations are variably saturated fluvial depositional systems characterized by shale and fine6, medium6, and coarse6grained sandstone sequences. Lithology is highly variable and difficult to correlate from borehole data. No laterally continuous confining layers of shale exist below the maximum depth of ground6water use to retard upward solute migration. A comprehensive review of regional and local geology is provided in SI Section A.

Domestic wells in the Pavillion area draw water from the Wind River Formation 6 a major aquifer system in the WRB[18,19] From the surface to approximately 30 m bgs, ground water exists under unconfined conditions[20]. Below this depth, ground water is present in lenticular, discontinuous, confined sandstone units with water levels well above depths of water producing zones and in some instances flowing to the surface[18,20,21] indicating the presence of strong localized upward gradients. The majority of documented domestic well completions in Fremont County[21] and five municipal wells in the Town of Pavillion[22] west of the Field are completed in the Wind River Formation.

Flow to the surface was observed in a domestic well during the Phase II sampling event[6] and at 4 production wells during bradenhead testing in 2012 (SI Section D.3). While the overall vertical ground6 water gradient in the Pavillion Field is downward, these observations indicate that localized upward hydraulic gradients exist in the Field relevant to potential upward solute migration. The deepest domestic wells in the Pavillion Field and immediate surrounding area are 229 m and 322 m bgs, respectively (Table

SI B1). Two municipal wells were proposed, but not drilled, in the Pavillion Field as replacement water for domestic wells at depths of 305 m bgs[22].

Major ion concentrations of domestic wells in the Pavillion field analyzed here are typical for the Wind River Indian Reservation (WRIR) west of the Pavillion Field and Fremont County (Table 1). The Fort Union Formation is not used for water supply in the Pavillion area. However, the formation is highly productive and permeable where fractured[19] with TDS values from 1,000 to 5,000 mg/L[23]. The Wind River and Fort Union Formations in the Pavillion Field therefore meet the definition of USDWs, as explicitly stated by EPA[7,24] and usable water as defined in federal statutes. Domestic well construction and major ion concentrations for individual domestic wells are summarized in Tables SI B1, and SI B2, respectively.

Table 1. Summary of major ion concentrations of domestic wells in the Wind River Indian Reservation (WRIR), Fremont County, WY, and within and around the Pavillion Field

	WRIR[a]			**Fremont County[b]**			**Within and Around Pavillion Field[c]**		
Parameter (mg/L)	**n**	**median**	**range**	**n**	**median**	**range**	**n**	**median**	**range**
TDS	154 49	0	21165110	77 103	0 24865100	65 925† 22	9†		64901†
Ca	149 10		16486 77 4	5		1.76380 4	8 50.8		3.326452
Mg	128 2.	2	0.16195 77	8.2		0.095699 4	5 5.32		0.024647
Na	153 15	0	561500 77	285		4.561500 7	2 260		38.061290
K	NA N	A	NA	77 2.	45	0.1630 43	1.36		0.179610.5
SO_4	154 20	1	263250 77	510		1263300 8	8 590		29.063640
Cl	154 14		26466 77 2	0		36420 48	21.1		2.60677.6
F	154 0.	7	0.168.8 76	0.9		0.264.9 46	0.88		0.2064.1

a – From Daddow[18]
b – From Plafcan et al.[21]
c – Major ion concentrations in domestic wells provided in Table SI B2.
n 6 Number of locations. Mean values used for multiple sampling events
† 6 TDS for EPA data estimated using linear regression equation from Daddow[18] TDS= 0.785*SC6130 (n=151, r^2=0.979)
NA – Not available

Well Stimulation Depths, Treatments, and Chemical Additives

Exploration of oil and gas in the Pavillion Field commenced in August 1953 with increasing shallow stimulations through time (Figure 2). The first acid stimulation and hydraulic fracturing stage (injection over one or more discrete intervals) occurred in June 1960 and October 1964, respectively. The last stimulation stage (hydraulic fracturing) occurred in April 2007. Most production wells were completed and stimulated during several periods of increased activity, especially after 1997 (Figure 2a). Acid stimulation and hydraulic fracturing occurred as shallowly as 213 m and 322 m bgs, respectively, at comparable depths to deepest domestic wells in the area (Figure 2a). More than half of the stimulation stages were < 1 km from the surface. Approximately 10% of stimulation stages occurred within 550 m bgs or within 250 m of deepest ground use (Figure 2b). Surface casing – the primary line of defense to protect ground water during conventional and unconventional oil and gas extraction – is relatively shallow in the Pavillion field with a median depth and range of 185 m (shallower than the deepest ground water use) and 1006706 m bgs, respectively (FigureSI C1). A summary of production well construction is provided in Table SI C1. There is no primary cement often hundreds and sometimes thousands of meters below surface casing (Figure SI CI).

A comprehensive summary of available information on well stimulation in the Pavillion Field is provided in Table SI C2. With the exception of two stimulation stages in 2001, acid stimulation ceased in 1999. Use of hydrofluoric acid, associated with matrix acidizing[25], was documented at two production wells. Overlap in instantaneous shut in pressures (wellhead gauge pressure immediately following fracture treatment) between acid stimulation and hydraulic fracturing (Figure SI C2) and "breakdown pressures" documented during acid stimulation suggest that both matrix and acid fracturing without proppants occurred in the Pavillion Field.

Acidizing solutions used in the Field typically consisted of 7½% or 15% hydrochloric acid solution plus additives described as inhibitors, surfactants, diverters, iron sequestration agents, mutual solvents, and clay stabilizers. Acidizing solutions were often flushed with a 2, 4, or 6% potassium chloride (KCl) solution. Pad acid contained 10650%heavy aromatic petroleum naptha. Corrosion inhibitors contained isopropanol and propargyl alcohol. Clay stabilizers contained methanol. Musol solvents used for acid stimulation consisted of 606100% 26butoxyethanol (26BE) and 10630% oxylated alcohol (Table SI C3).

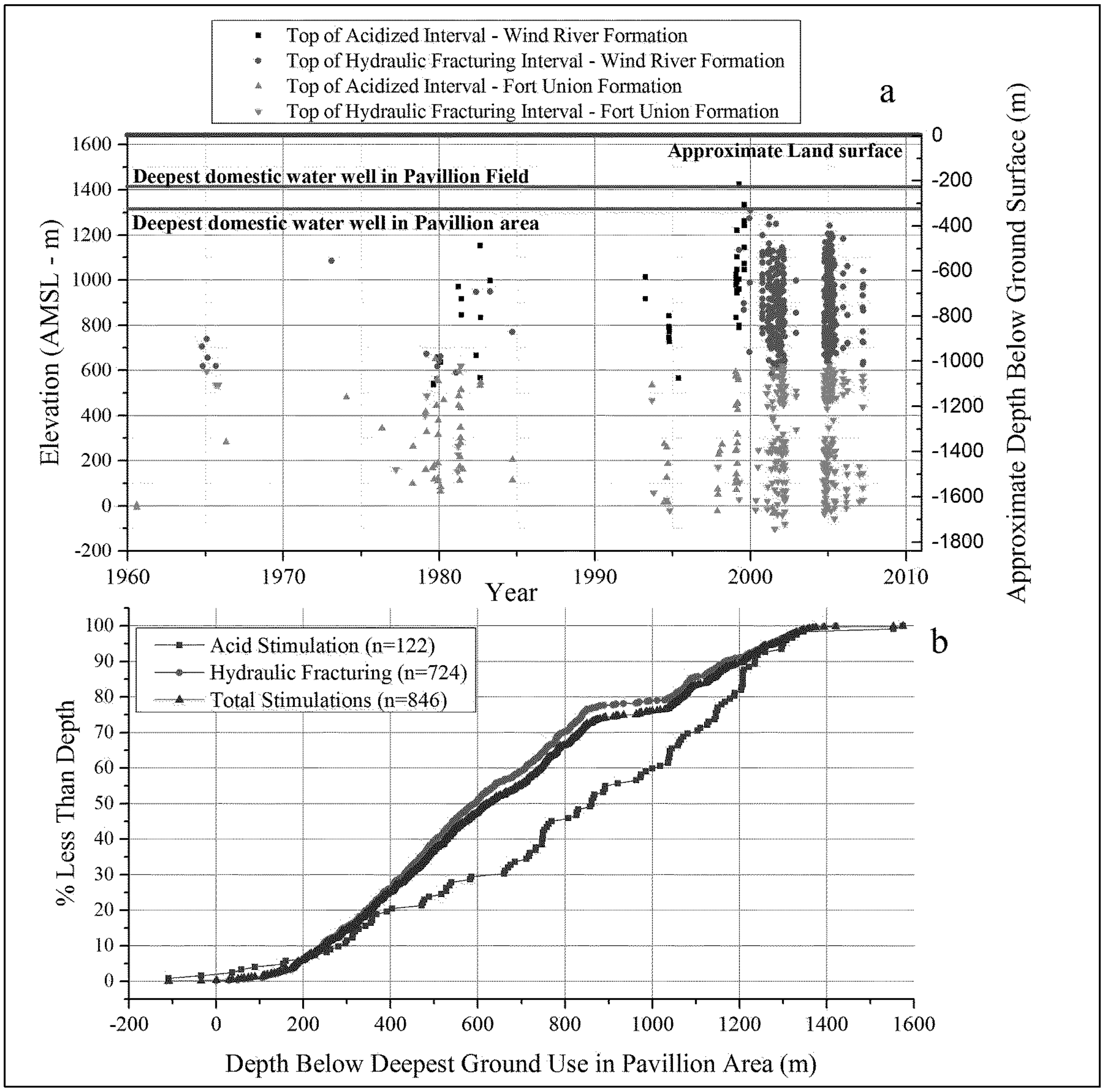

Figure 2. (a) Top elevation in absolute mean seal level (AMSL) of documented acid and hydraulic fracturing stimulation stages as a function of time. (b) Cumulative distribution of stimulation stages as a function of depth below deepest ground water in the Pavillion area. Note: documentation of stimulation stages is absent in a number of well completion reports indicating numbers presented here are a lower bound.

Prior to 1999, salt solutions (e.g., 2, 4, or 6% KCl) were commonly used for hydraulic fracturing. After 1999, a 6% KCl solution was used extensively for hydraulic fracturing often combined with CO_2 foam, with subsequent flushing using a KCl solution. Sodium chloride was used as an "additive." Undiluted diesel fuel was used for hydraulic fracturing at three wells prior to 1985. From the mid‑1970s through 2007, there was widespread use of gelled fracture fluids (gelled water, linear gel, and cross‑linked gel). Diesel fuel #2 was used for liquid gel concentrates. Ammonium chloride, potassium hydroxide, potassium metaborate, and a zirconium complex were used as crosslinkers.

Gelled fracture fluids were used extensively with CO_2 foam (Table SI C4). Between 2001 and 2005, “WF6125” was used with CO_2 foam (often with a 6% KCl solution) for hydraulic fracturing (Table SI C5). A stimulation report (one of only three publically available throughout the operating history of the Field) indicates that WF6125 contained diesel fuel#2, 26BE, isopropanol, ethoxylated linear alcohols, ethanol, and methanol. During 2001, WF6125 and unidentified product mixtures were used with a 6% KCl and a 10% methanol solution and CO_2 foam for hydraulic fracturing followed with a 6% KCl and 10% methanol solution flush. Other WF6series compound mixtures of unknown composition were also used with CO_2 foam and in some cases with nitrogen. Methanol, isopropanol, glycols, and 26BE were used in foaming agents. Ethoxylated linear alcohols, isopropanol, methanol, 26BE, heavy aromatic petroleum naptha, naphthalene, and 1,2,46trimethylbenzene were used in surfactants with CO_2 foam. Slickwater (commonly with a 6% KCl solution) was used for hydraulic fracturing with and without CO_2 foam in 2004 and 2005, respectively (Table SI C6).

Evaluation of Impact to USDWs and Usable Water

In the Pavillion Field, impacts of well stimulation to USDWs and usable waters depends upon the interactions of compounds used for well stimulation with water bearing units, particularly sandstone units at or near water saturation. Significant water bearing units exist throughout the Wind River and Fort Union Formations in the Pavillion Field. For instance, production well Unit 41X610 was recommended for plugging and abandonment in 1980 because of “problems with water production and casing failure.” In 1980, drilling logs at Tribal Pavillion 1462 stated "Hit water flow while drilling at 410564109 ft”bgs. The magnitude of produced water production in the Pavillion Field is highly variable with some wells having produced ≥ 100,000 barrels (bbls) (1 bbl = 42 gallons or ~ 160 L) of water (e.g., Tribal Pavillion 23610). In some cases, stimulation fluids were injected directly into water bearing units. For instance, at

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Tribal Pavillion 1461, a cast iron bridge plug wasused to stop water production in 1993 from an interval where hydraulic fracturing occurred using undiluted diesel fuel in 1964.

Stimulation fluid migration or solute transport to water sandstone bearing units in the Pavillion Field also likely occurred during fracture propagation and subsequent leakoff (loss of fluid into a formation in or near the target stratum). Leakoff increases in the presence of complex induced fracture configurations and in contact with more permeable sandstone units[26629]. Such conditions are expected in heterogeneous fluvial media in the Pavillion Field. Leakoff can remove much or most of the fracturing fluid even for moderate sized induced fractures[26,27]. Also, hydraulic gradients during produced water recovery are minimal compared to pressure buildup during stimulation in the Pavillion Field making full recovery of stimulation fluids unlikely[3,30]. Maximum ISIP values for acid stimulation and hydraulic fracturing were 19.5 and 40.1 MPa (Figure SI C2), respectively.

The migration of stimulation fluids to water bearing units also likely occurred at some production wells as a result of loss of zonal isolation particularly through boreholes outside of production casings. Examples of potential loss of zonal isolation at 11 production wells is discussed in SI Section D.1. Casing failure was documented at 5 production wells. Cement squeezes were performed at 6 production wells above stimulation intervals within days of stimulation. Reasons for remedial cement squeezes were not provided in well completion reports[31]. At one production well, stimulation fluid was injected just 4 m below an interval lacking cement outside of the production casing with maximum stimulation pressure documented as only 1.3 MPa indicating little resistance to flow.

Major ion concentrations in produced water (Table SI D1) were distinct from values expected in the Wind River Formation (Table 1). Major ion concentrations were similar in domestic wells less than and greater than 1 km from production wells (Figure 3) indicating that datasets for domestic wells could be combined for statistical comparison to produced water samples. Sodium, potassium, and chloride concentrations were significantly higher and sulfate concentrations significantly lower in produced water compared to domestic wells at Mann6Whitney p6valuesof 6.6E619, 2.1E615, 2.6E616, and 4.4E619 respectively providing direct evidence of impact to USDWs at depths of stimulation.

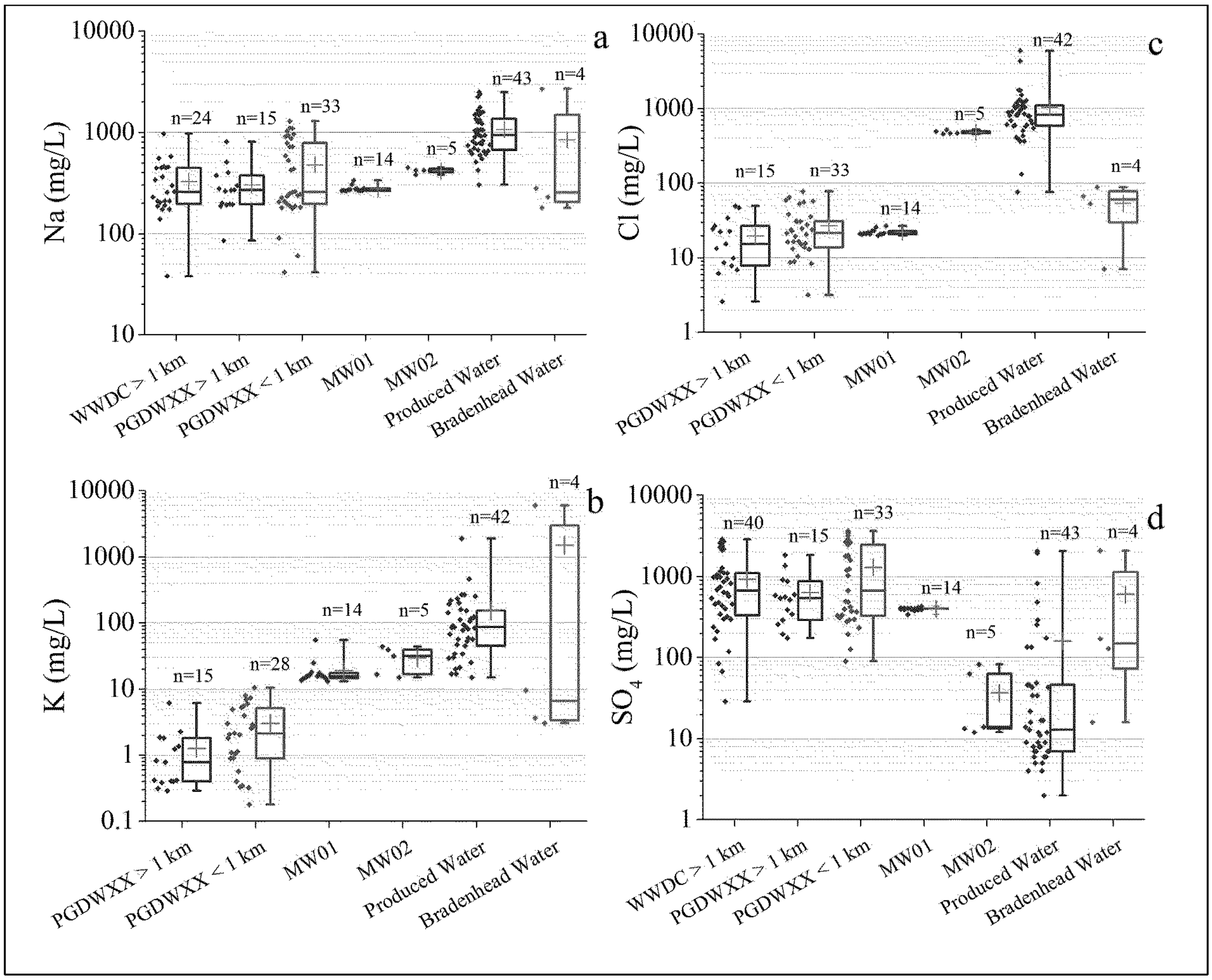

Figure 3. Box and whisker plots of minimum and maximum, quartiles, median (line in boxes), mean (crosses in boxes) of (a) Na, (b) K, (c) Cl, (d) SO4 for domestic wells sampled by EPA (PGDWXX series) greater than and less than 1 km from a production well, Wyoming Water Development Commission (WWDC series) greater than 1 km from a production well, EPA monitoring wells MW01, MW02, produced water, and bradenhead water samples. For domestic wells sampled more than once are represented once with a mean value. Data points at MW01 and MW02 represent samples collected during Phase III, IV, and V sample events. Major ion concentrations for produced and bradenhead water are provided in Table SI D1 and in Tables SI E2b and SI E3b for MW01 and MW02 respectively.

Produced water samples were collected from gas6water separators at four production wells and analyzed for organic compounds (Table SI D3, Figure SI D1) during the Phase II sampling event[6]. Samples from one production well appeared to be from both an aqueous and an apparent non6aqueous phase liquid with the latter exhibiting thousands of mg/L of benzene, toluene, ethylbenzene, xylenes (BTEX). Synthetic organic compounds methylene chloride and triethylene glycol (TEG) were detected in produced water samples at 0.51 and 17.8 mg/L, respectively indicating anthropogenic origin. Methylene chloride has been detected in flowback water in other systems[32], in 122 domestic wells above the Barnett Shale[33], and in air sampled near well sites[34].

Sample Results at MW01 and MW02

Major ion concentrations outside expected values in the Wind River Formation (Figure 3, Tables SI E3b, SI E4b) and detection of organic compounds (Figure 4, Tables SI E3a, SI E4a) in EPA monitoring wells known to have been used for production well stimulation indicates upward solute migration to depths of current ground water use. Maximum concentrations of potassium in MW01 and MW02 were 54.9 and 44.0 mg/L, respectively, higher than potassium concentrations in domestic wells which are representative of expected values in the Wind River Formation (Table 1).

It is possible that observation of elevated potassium in EPA monitoring wells was attributable to release of potassium oxides and sulfates in cement used for monitoring well construction (SI Section E6), however, potassium was detected in a bradenhead water sample at 6,000 mg/L indicative of high potassium concentrations at depths below EPA monitoring wells due to well stimulation. The median chloride concentration at MW02 was 469 mg/L (Figure 3), well above concentrations in domestic wells representative of expected values in the Wind River Formation. Compounds containing chlorides (e.g., KCl solutions) were used extensively for stimulation throughout the stimulation history of the Field.

Diesel range organics (DRO) and gasoline range organics (GRO) were detected in both monitoring wells with maximum concentrations in MW02 at 4,200 and 5,290 Zg/L, respectively (Figure 4). As discussed previously, petroleum products, including diesel fuel, were used for well stimulation in the Pavillion Field. Benzene, toluene, ethylbenzene, m,p6xylenes, and o6xylene were detected in MW02 at maximum concentrations of 247, 677, 101, 973, and 253 Zg/L respectively. The maximum contaminant level (MCL) of benzene is 5 µg/L, fifty times lower than the observed value. Unlike in MW02, MW01 did not have detectable BTEX compounds, possibly due to biodegradation of these compounds at the shallower depth of this well or that upward migration of BTEX did not occur at this location. Detection of BTEX compounds in MW02 may be the result of gas6water partitioning of BTEX compounds intrinsically present in natural gas. BTEX compounds were present in string and bradenhead gas (Table SI D2). However, we could find no published information on BTEX compounds in ground water at concentrations of this magnitude naturally occurring above a gas field.

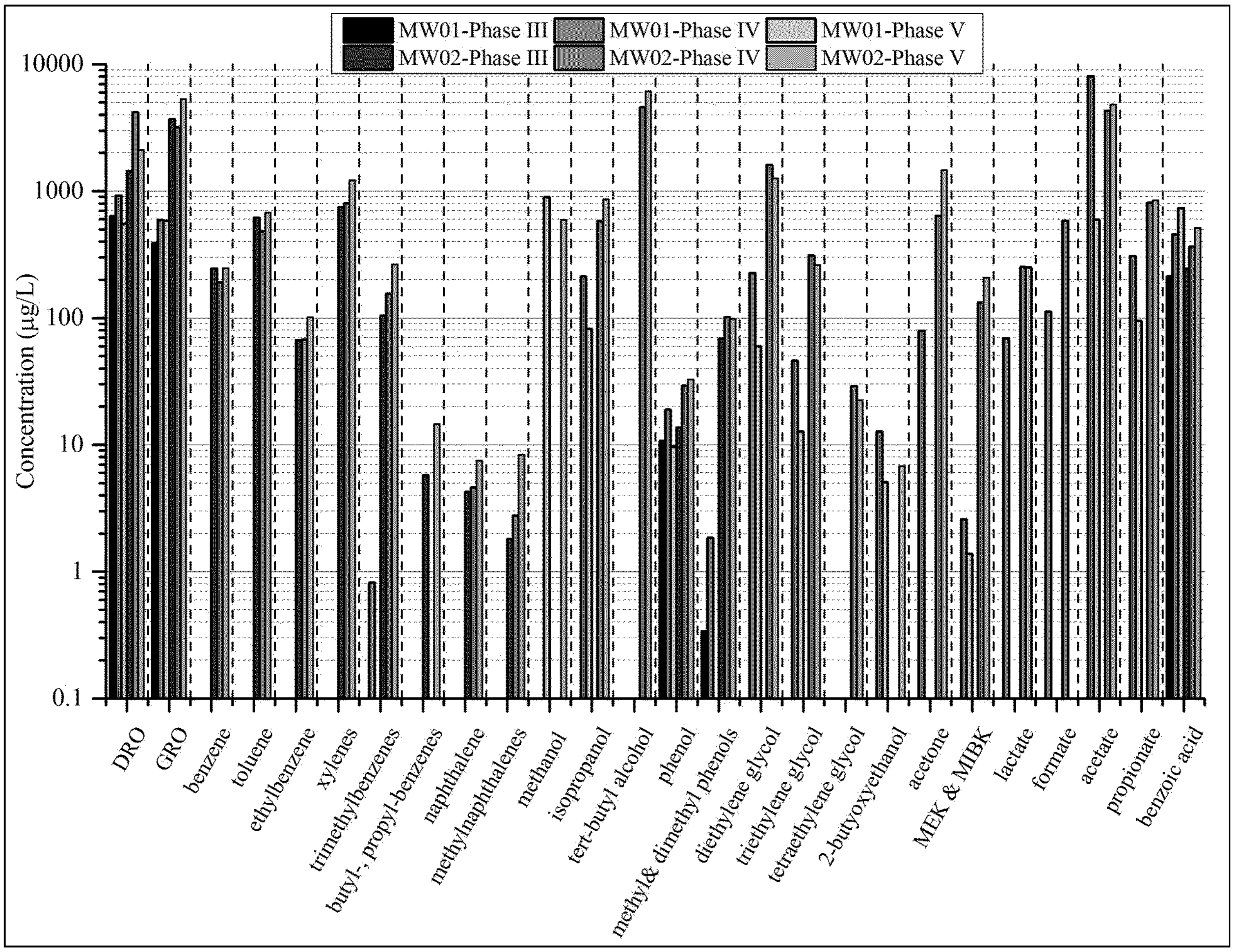

Figure 4. Summary of organic compounds detected by EPA in MW01 and MW02 during Phase III, IV, and V sampling events. Glycols, alcohols, and low molecular weight organic acids not analyzed in Phase III. Alkylphenols and methanol (GC6FID method) only analyzed in Phase V. Organic compounds detections for MW01 and MW02 are summarized in Table SI E3a and Table SI E4a, respectively.

1,3,56, 1,2,46, and 1,2,36Trimethylbenze were detected at maximum concentrations of 71.4, 148, 45.8 Zg/L respectively in MW02 and at order of magnitude lower concentrations in MW01. Naphthalene, methylnaphthalenes, and alkylbenzenes were also detected in MW02 at concentrations up to 7.9, 10.2, and 21.2 Zg/L, respectively. Similar to BTEX compounds, detection of trimethylbenzenes, alkylbenzenes, and naphthalenes could reflect non6anthropogenic origin but natural gas from the Pavillion Field and in EPA monitoring wells is “dry” (ratio of methane to methane through pentane concentration > 0.95) (SI Section A.2, Table SI E5) so the detection of higher molecular weight hydrocarbons in ground water due to natural gas migration is unexpected. Trimethylbenzenes and naphthalenes were present in compounds used for well stimulation (Table SI C3).

Other organic compounds used extensively for well stimulation were detected in MW01 and MW02 (Figure 4). Methanol, ethanol, and isopropanol were detected in monitoring wells at up to 863, 28.4, and 862 respectively µg/L (Figure 4). *Tert*6butyl alcohol (TBA) was detected at 6,120 Zg/L in MW02. Detection of TBA in ground water has been associated with degradation of *tert*6butyl hydroperoxide used for hydraulic fracturing[35]. Another potential source of TBA is degradation of methyl *tert*6butyl ether (MTBE) associated with diesel fuel[36640].

Diethylene glycol (DEG) and TEG were detected in both monitoring wells at maximum concentrations of 1570 and 310 Zg/L, respectively (Figure 4). Tetraethylene glycol was detected only in MW02 at 27.2 Zg/L. MSDSs indicate that DEG was used for well stimulation. A MSDS was provided for TEG but use of this compound was not specified. Polar organic compounds, including DEG, are commonly used as cement grinding agents. Similar to elevated potassium detection, it is possible that detection of glycols in aqueous samples from EPA monitoring wells could be attributable to release of glycols from cement used for monitoring well construction, however, mass flux scenario modeling common to testing of materials in contact with drinking waters indicates that this is unlikely (SI Section E.7). The compound 26BE, a glycol ether used extensively for well stimulation, was detected in both monitoring wells at a maximum concentration of 12.7 Zg/L. It is unlikely that cement interaction caused detection of 26BE (SI Section E.7).

The low molecular weight organic acids (LMWOAs) lactate, formate, acetate, and propionate were detected in both monitoring wells at maximum concentrations of 253, 584, 8050, and 844 Zg/L, respectively (Figure 4). LMWOAs are anaerobic degradation products associated with hydrocarbon contamination in ground water[41,42]. Acetate has been detected in produced water[43645] in impoundments used for flowback from the Marcellus Shale[46], and in produced water from the Denver6Julesburg Basin[47]. Acetate and formate were detected in flowback water from two different fracturing sites in Germany with investigators concluding that these compounds were likely of anthropogenic origin resulting from degradation of polymers used in the fracturing fluid[48]. Benzoic acid which is associated with the degradation of aromatics, was also detected in both monitoring wells at a maximum concentration of 513 Zg/L.

Phenols were detected in both monitoring wells with maximum concentrations of phenol, 26 methylphenol, 3&46methylphenol, and 2,46dimethylphenol at MW02 at 32.7, 22.2, 39.8, and 46.3 Zg/L, respectively. Ketones were also detected in both monitoring wells with maximum concentrations of acetone, 26butanone (MEK), and 46methyl626pentanone (MIBK) at MW02 at 1460, 208, and 12.5 Zg/L, respectively. Acetone, MEK, phenol, 26methylphenol,3&4 methylphenol, and 2,46dimethylphenol were detected in produced water from the Denver6Julesburg Basin[47]. MIBK, MEK, and acetone may result from microbial degradation of biopolymers used for hydraulic fracturing[47]. Nonylphenol and octylphenol, commonly associated with ethoxlyated alcohols, were detected in both monitoring wells with maximum concentrations at MW02 at 28 and 2.9 Zg/L, respectively. Ethoxlyated alcohols were used for well stimulation in the Pavillion Field.

Assessment of Potential Impact of Unlined Pits to Domestic Wells

EPA[7] previously reported disposal of diesel fuel6based (invert) drilling mud and production fluids (flowback, condensate, produced water) in unlined pits and resultant ground6water contamination in surficial Quaternary deposits but did not document the extent of these disposal practices. Unlined pits were used or disposal of drilling mud and production fluids. Unlined pits were emptied and closed in 1995[49,50]. Water6based drilling mud was disposed in lined and unlined pits at 33 and 7 locations, respectively (Table SI F1). Invert mud, consisting of up to 79% diesel fuel was disposed in unlined pits at 57 locations.

There are at least 44 unlined pit locations where disposal of production fluids was explicitly described in well completion reports or where production and well stimulation occurred prior to 1995 with likely disposal of production fluids in unlined pits. A comprehensive and detailed summary of information available on disposal of drilling mud and production fluids in pits, results of soil and ground6 water sampling, excavation volumes and associated criteria (1,000 to 8,500 mg/kg total petroleum hydrocarbons), proximity and direction of unlined pits to domestic wells, and recommendations by WOGCC[15] for further investigation (or no investigation) is provided in Table SI F2. Eight pit locations are in WY Voluntary Remediation Program – a coordinated voluntary effort between WYDEQ and Encana to remediate soil and ground6water contamination.

Encana has collected ground water samples in surficial Quaternary deposits at 12 unlined pit locations[15]. The highest reported concentrations of GRO and DRO were 91,000 and 78,000 Zg/L, respectively. Benzene, toluene, ethylbenzene, and xylenes were detected at 5 locations at concentrations up to 1,960, 250, 240, and 1,200 Zg/l, respectively. Sample results indicate impact to surficial ground water in Quaternary deposits. Given use of flood irrigation for hay production and locally induced downward ground6water hydraulic gradients at many pit locations, ground6water contamination in the underlying Wind River Formation is plausible and necessitates further investigation. There are currently no monitoring wells in the Wind River Formation in the vicinity of unlined pits.

There may be as many as 48 domestic wells with 600 m of unlined pits of which only 22 were sampled by EPA for DRO and of which 11 were resampled by WYDEQ[13] (Table SI F3). DRO concentrations in domestic wells <600 m from unlined pits receiving production fluids were elevated (p value = 0.003 in Mann6Whitney test) compared to domestic wells > 600 m from unlined pits (Figure 5a). DRO was detected at 752 mg/kg in a reverse osmosis filter sample from PGDW20 during the Phase II sampling event (Table SI F3). Concentrations of DRO in domestic wells generally decreased with depth (Figure 5b). 26BE, a compound used extensively forwell stimulation, was detected at 3,300 Zg/L in a domestic well[13] (Table SI F3). The depth of this domestic well is only 9.1 m bgs and is located within 134 m of an unlined pit used for disposal of production fluids. Other compounds associated with production well stimulation (e.g., isopropanol) were detected at lower concentrations in other domestic wells (Table SI F3)

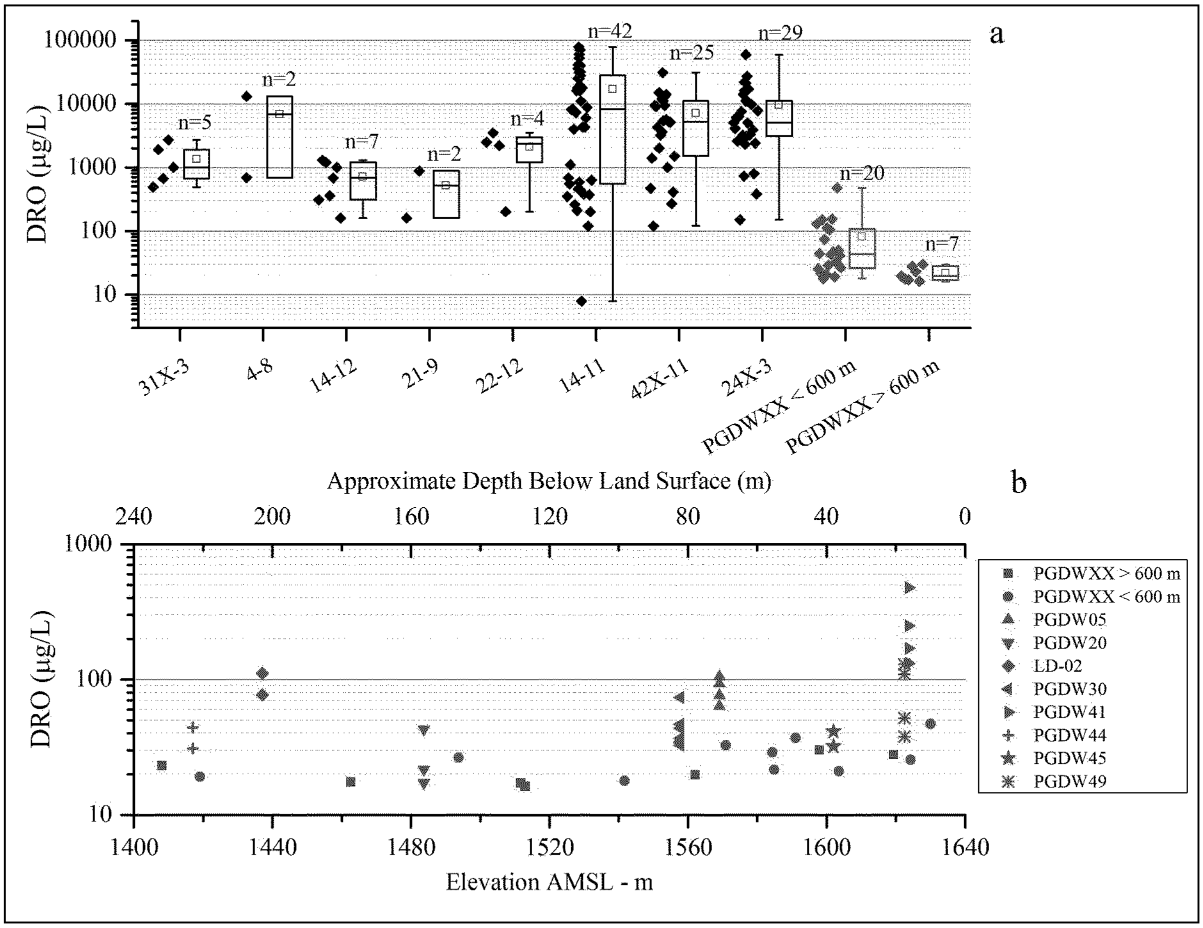

Figure 5. (a) Box and whisker plots of minimum and maximum, quartiles, median (line in boxes), mean (squares in boxes) of diesel range organics (DRO) in shallow monitoring wells near unlined pits potentially receiving production fluids (abbreviations of production wells in Table SI C1) and domestic wells (PGDWXX series) less than and greater than 600 m from pits. (b) DRO as a function of elevation for domestic wells with concentration variation illustrated for domestic wells sampled during more than once. Land surface is approximated at 1640 m AMSL.

At two domestic wells (PGDW05 and PGDW30), chromatograms for DRO analysis suggest a diesel fuel source (Figure SI F2a, b). Chromatograms of aqueous (Figure SI F3a) and carbon trap samples (Figure SI F3b) for DRO at another domestic well (PGDW20) indicated the presence of heavy hydrocarbons in water. All three domestic wells are located near unlined pits used for disposal of production fluids.

Adamantanes were detected at low aqueous concentrations (< 5 Zg/L) at a 4 domestic wells (PGDW05, PGDW20, PGDW30, and PGDW32) (Table SI F3). Admantane, 26methyl adamantane, and 1,36dimethyladamantane were detected in a reverse osmosis filter sample at PGDW20 at concentrations of 420, 9,400, and 2960 µg/kg, respectively. Adamantanes were detected in produced water up to 74 mg/L (Table SI D3. Figure SI D1) indicating potential disposal in unlined pits. The inherent molecular stability of admantanes and other diamondoid compounds imparts thermal stability resulting in enrichment in manufactured petroleum distillates[51]. Diamondoids are resistant to biodegradation[52,53] resulting in their use as a fingerprinting tool to characterize petroleum and condensate induced ground6 water contamination[54]. Sample results at domestic wells indicate potential impact from unlined pits and the need for further investigation.

Previous investigations and our new data for the Pavillion Field highlight some take6home messages for unconventional oil and gas extraction. First, while EPA[3] previously documented stimulation into USDWs (limited to CBM development), we have, for the first time, demonstrated inorganic and organic solute contamination to USDWs as a result of this activity. As a result of exemption from the Safe Drinking Water Act, hydraulic fracturing into USDWs is currently allowable in the United States with resultant impact to USDWs. Stimulation into USDWs is common during CBM recovery and occurs to some unknown extent in tight gas formations, with such development accelerating. Investigations need to be conducted at other locations where hydraulic fracturing is occurring into USDWs to evaluate local and regional water resource impact as result of this activity especially in areas vulnerable to sustained drought exacerbated by climate change.

Secondly, in the Pavillion Field, well stimulation occurred many times less than 500 m from the surface and, in rarer cases, at the same depths as the deepest drinking water in the area (Figure 2). Very shallow hydraulic fracturing, poses greater risks than deeper fracturing does[55]. Shallow fractures[56] and poor well integrity issues[57,58] have been shown to lead to issues of groundwater contamination elsewhere.

Finally, detection of DRO and other organic compounds detected in domestic wells could be due to disposal of flowback, condensate, and produced water from at least 44 unlined pits used prior to the mid 1990's. Additional investigation, including installation of monitoring wells in the Wind River Formation, is necessary to determine the full extent and risk posed to domestic well users from unlined pits at the Pavillion Field and elsewhere.

ASSOCIATED CONTENT

Supplemental discussion and tables summarizing datasets are provided in the Supporting Information (SI) portion of the paper.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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